

LABORATORY DETECTION OF THE C_3N AND C_4H FREE RADICALS

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ABSTRACT

The millimeter-wave spectra of the linear carbon chain free radicals C_3N and C_4H , first identified in IRC +10216 and hitherto observed only in a few astronomical sources, have been detected with a Zeeman-modulated spectrometer in laboratory glow discharges through low pressure flowing mixtures of $N_2 + HC_3N$ and $He + HCCH$, respectively. Four successive rotational transitions between 168 and 198 GHz have been measured for C_3N , and five rotational transitions between 143 and 200 GHz for C_4H ; each is a well-resolved spin doublet owing to the unpaired electron present in both species. Precise values for the rotational, centrifugal distortion, and spin doubling constants have been obtained, which, with hyperfine constants derived from observations of the lower rotational transitions in the astronomical source TMC 1, allow all the rotational transitions of C_3N and C_4H at frequencies less than 300 GHz to be calculated to an absolute accuracy exceeding 1 ppm.

Subject headings: interstellar: molecules — laboratory spectra — line identifications — molecular processes — Zeeman effect

I. INTRODUCTION

The isoelectronic free radicals C_3N and C_4H were first identified in the circumstellar envelope of IRC +10216 (Guélin and Thaddeus 1977; Guélin, Green, and Thaddeus 1978) largely on the basis of theoretical arguments; neither had been observed in the laboratory, although trapped C_4H had been detected by electron spin resonance in a low-temperature inert gas matrix (Dismuke, Graham, and Weltner 1975). The lines detected were millimeter-wave high rotational transitions split into well-resolved spin doublets by the unpaired electron; hyperfine structure from the H or N nuclei—which collapses with increasing rotational quantum number—was far too small to observe. Astronomical confirmation of these identifications was subsequently obtained when the predicted hyperfine structure of the lower rotational transitions was detected in the very narrow line source TMC 1 in the Taurus dark clouds (Friberg *et al.* 1980; Bell, Sears, and Matthews 1982; Guélin, Friberg, and Mezaoui 1982).

We have now detected both C_3N and C_4H in the laboratory with a Zeeman-modulated spectrometer designed to study free radicals in a gas discharge. In addition to conclusively confirming the astronomical identifications, our laboratory measurements, when combined with the astronomical data, significantly improve several of the microwave constants of C_3N and C_4H and allow all the microwave lines of these mole-

cules to be calculated to the accuracy required by radio and submillimeter-wave astronomy.

II. OBSERVATIONS

a) Apparatus

The spectrometer used to detect C_3N and C_4H was that used recently to detect CCH (Gottlieb, Gottlieb, and Thaddeus 1983), with the addition of a Zeeman coil and the installation of a more powerful minicomputer (Nova 4) for experiment control and data analysis. Klystron modulation and second harmonic detection, as before, were used to suppress noise, and in addition a second modulation was applied by switching on a magnetic field (11 G) with the Zeeman coil on alternate klystron sweeps. The resulting difference spectrum is, as Figure 1 shows, free of lines from closed shell molecules present either as contaminants or produced in the discharge, and is largely free of baseline distortion from standing waves.

b) Free Radical Production

The C_3N radicals were produced in a room temperature DC discharge (0.2 A) through a flowing mixture of HC_3N (cyanoacetylene) and either N_2 or He, the former yielding a more stable discharge and being therefore the production scheme that was preferred. A roughly equal

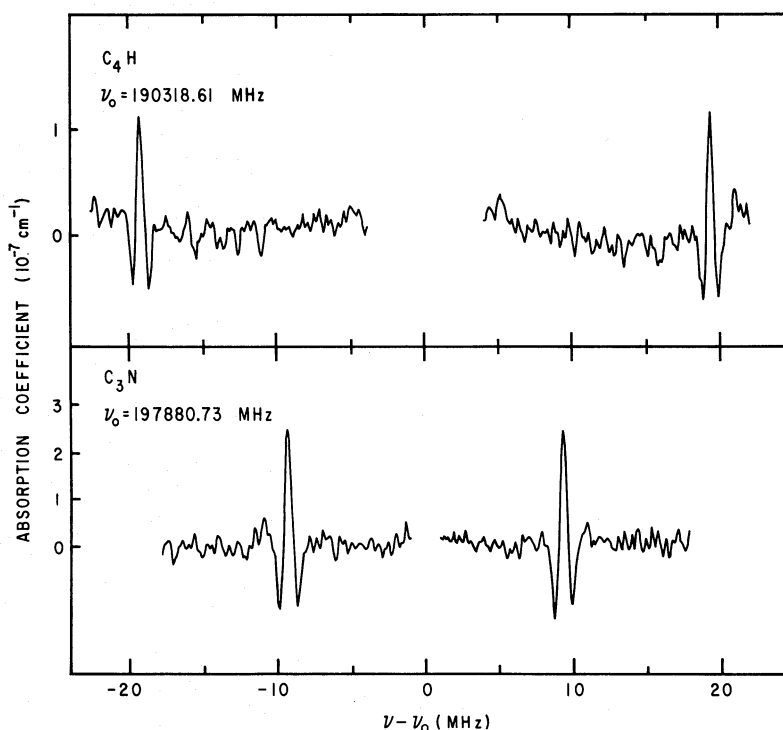


FIG. 1.—Sample data: the $N=19 \rightarrow 20$ rotational transitions of C_4H and C_3N . Simultaneous frequency and Zeeman modulation have been used to suppress noise and to provide flat baselines; the line shape is approximately the second derivative of a Lorentzian. The total integration time for each spectrum was ~ 60 minutes.

molar mixture of HC_3N and N_2 at a total pressure of 25 mtorr gave the best yield of C_3N . The HC_3N was synthesized from methyl propiolate (Columbia Chemical) by the procedure described by Murahashi *et al.* (1956), and was shown by 1H NMR to be more than 98% pure; it could be stored at $-5^\circ C$ for several months without evidence of polymer formation and did not require vacuum distillation prior to use. The flow rate of HC_3N was ~ 0.4 g hr^{-1} . As a result of the discharge, a brown polymer slowly deposited on the walls of the spectrometer cell and the microwave lenses, but its millimeter-wave loss was so small that the system required cleaning only after many days of operation.

The C_4H radicals were produced in a liquid nitrogen-cooled DC discharge (0.3 A) through a mixture of C_2H_2 (acetylene) and either He or Ar. A roughly 2 to 1 molar mixture of C_2H_2 and He at a total pressure of ~ 25 mtorr gave the best yield of C_4H , the discharge conditions yielding the strongest C_4H lines being similar to those under which the strongest CCH lines had previously been observed. The Ar discharge yielded lines that were nearly as strong. The buildup of wall deposit in either discharge was somewhat more rapid than in that producing C_3N , and required removal after 10 to 20 hr of operation.

The line widths (half-width at half-intensity) were typically 550 kHz for C_3N and 600 kHz for C_4H , and

resulted mainly from pressure broadening. The Doppler-broadened HWHM was ~ 175 kHz for C_3N and 100 kHz for C_4H , and the effective Zeeman HWHM from the terrestrial magnetic field was only ~ 70 kHz.

Absorption coefficients were calibrated by comparing the lines of C_3N and C_4H with that of $^{18}O^{13}CS$ at 182,096 MHz in normal abundance without Zeeman modulation. Concentrations of 4×10^9 cm^{-3} for C_3N and 1.3×10^{10} cm^{-3} for C_4H were derived from the measured absorption coefficients by using the ab initio dipole moments calculated by Wilson and Green (1977) and by assuming a kinetic temperature of 300 K for C_3N and 100 K for C_4H .

The C_4H mole fraction of 3×10^{-6} is comparable to the fractional ionization deduced from measurements of HCO^+ under similar discharge conditions, and is therefore consistent with the C_4H being produced by ion-molecule reactions. The initial process that occurs in the acetylene discharge (Vasile and Smolinsky 1977) is the ionization of C_2H_2 followed by the reaction of $C_2H_2^+$ with C_2H_2 to form $C_4H_2^+$ and $C_4H_3^+$. A possible mechanism for C_4H formation is the dissociative recombination of either $C_4H_2^+$ or $C_4H_3^+$. Cleavage of C_2H_2 is not a major process; therefore, carbon chain molecules with an odd number of carbon atoms such as C_3H^+ are not formed. There is a high conversion of C_2H_2 to nonvolatile products because of the tendency of the acetylenic

TABLE 1
LABORATORY C₃N AND C₄H FREQUENCIES

$N \rightarrow N'$	C ₃ N		C ₄ H	
	Measured Frequencies (MHz)	Measured – Calculated (MHz)	Measured Frequencies (MHz)	Measured – Calculated (MHz)
14 → 15	142,728.773 ± 0.018	– 0.010
	142,767.280 ± 0.016	0.013
16 → 17 ...	168,194.938 ± 0.016	0.015
	168,213.682 ± 0.015	0.006
17 → 18 ...	178,087.395 ± 0.011	0.001	171,272.249 ± 0.014	– 0.011
	178,106.141 ± 0.012	– 0.006	171,310.707 ± 0.013	0.006
18 → 19 ...	187,979.515 ± 0.013	– 0.024	180,786.031 ± 0.017	– 0.003
	187,998.291 ± 0.012	– 0.002	180,824.472 ± 0.016	0.011
19 → 20 ...	197,871.353 ± 0.012	0.011	190,299.425 ± 0.014	0.009
	197,890.101 ± 0.013	0.005	190,337.804 ± 0.013	– 0.023
20 → 21	199,812.391 ± 0.016	0.006
	199,850.787 ± 0.015	0.008

NOTE.—For each rotational transition $N \rightarrow N'$ the first frequency listed is that of the $J = N + \frac{1}{2}$ spin component, the second that of $J = N - \frac{1}{2}$. Uncertainties are 1 σ , as discussed in § II c.

TABLE 2
MICROWAVE CONSTANTS OF C₃N AND C₄H (in MHz)

Molecular Constant	Laboratory (this work)	Astronomical (Guélin <i>et al.</i> 1982)	Laboratory Plus Astronomical (recommended constants)
C ₃ N			
B	4947.6208 ± 0.0011	4947.6190 ± 0.0009	4947.6207 ± 0.0011
$D \times 10^3$	0.7536 ± 0.0016	0.68 ± 0.06	0.7535 ± 0.0016
γ	– 18.730 ± 0.080	– 18.743 ± 0.004	– 18.744 ± 0.006
$\gamma_D \times 10^3$	– 0.023 ± 0.076	...	– 0.006 ± 0.011
b	– 2.16 ± 0.05	– 2.15 ± 0.03
c	2.85 ± 0.10	2.84 ± 0.09
eQq	– 4.34 ± 0.13	– 4.32 ± 0.10
C ₄ H			
B	4758.6557 ± 0.0007	4758.6567 ± 0.0007	4758.6557 ± 0.0007
$D \times 10^3$	0.8626 ± 0.0010	0.90 ± 0.03	0.8627 ± 0.0010
γ	– 38.648 ± 0.050	– 38.554 ± 0.004	– 38.555 ± 0.002
$\gamma_D \times 10^3$	0.202 ± 0.046	...	0.127 ± 0.009
b	– 19.09 ± 0.02	– 19.088 ± 0.006
c	12.43 ± 0.02	12.435 ± 0.010

NOTE.—Uncertainties are 1 σ derived from a least-squares fit.

ions to react readily with C₂H₂ to form yet longer carbon chains. Because C₂H₂ is so readily ionized or excited electronically, the electrons are prevented from becoming energetic enough to excite or ionize He or Ar which therefore merely act as diluents.

The C₃N mole fraction of 3×10^{-6} suggests that it too is formed by ion-molecule reactions. Unlike the acetylene discharge, little is known about HC₃N discharge chemistry. In an investigation of the reactions of 18 positive ions with HC₃N, Freeman, Harland, and

McEwan (1979) found that either H₂C₃N⁺ or HC₃N⁺ were produced in nearly all cases. It is possible that C₃N is formed from dissociative recombination of either H₂C₃N⁺ or HC₃N⁺, but the mechanism for its production in the discharge is really not understood.

c) C₃N and C₄H Measurements

The spin doublets of four successive rotational transitions of C₃N and five rotational transitions of C₄H were

TABLE 3
 THE MICROWAVE SPECTRA OF C_3N AND C_4H

C_3N					C_4H		
N+N'	J+J'	F+F'	Frequency (MHz)	Rel. Int.	F+F'	Frequency (MHz)	Rel. Int.
0+1	1/2+3/2	1/2+3/2	9884.288±0.040	0.12	0+1	9493.061±0.004	0.17
		3/2+5/2	9885.893±0.008	0.33	1+2	9497.616±0.002	0.42
		3/2+3/2	9886.097±0.032	0.10	1+1	9508.005±0.004	0.08
		1/2+1/2	9887.004±0.025	0.10
		3/2+1/2	9912.978±0.041	0.10	0+1	9547.961±0.005	0.08
1+2	1/2+1/2	1/2+3/2	9913.646±0.048	0.10	1+0	9551.717±0.004	0.08
		3/2+3/2	9915.455±0.017	0.12	1+1	9562.904±0.003	0.17
		3/2+5/2	19780.800±0.003	0.17	1+2	19014.720±0.002	0.23
		1/2+3/2	19780.826±0.004	0.10	2+3	19015.144±0.002	0.35
		5/2+5/2	19781.008±0.032	0.03	2+2	19025.107±0.004	0.03
	3/2+5/2	5/2+7/2	19781.094±0.003	0.27
		3/2+3/2	19783.546±0.042	0.03
		3/2+3/2	19797.478±0.030	0.05	1+1	19044.760±0.005	0.04
		1/2+3/2	19799.951±0.005	0.06	1+2	19054.476±0.002	0.21
		3/2+5/2	19800.121±0.003	0.17	0+1	19055.947±0.002	0.08
	3/2+3/2	1/2+1/2	19800.968±0.025	0.05
		5/2+5/2	19829.687±0.024	0.03	1+1	19099.656±0.006	0.02
		2+2	19119.761±0.005	0.04
		3/2+5/2	29676.137±0.008	0.13	2+3	28532.315±0.004	0.24
		5/2+7/2	29676.149±0.008	0.17	3+4	28532.466±0.004	0.32
2+3	5/2+7/2	7/2+9/2	29676.277±0.008	0.24
		5/2+5/2	29692.475±0.034	0.02	2+2	28561.816±0.005	0.03
		1/2+3/2	29694.989±0.010	0.07	2+3	28571.366±0.004	0.23
		3/2+5/2	29695.122±0.009	0.11	1+2	28571.531±0.005	0.15
		5/2+7/2	29695.143±0.008	0.18
	3/2+3/2	3/2+3/2	29696.002±0.039	0.02
		3+3	28675.986±0.007	0.02
		5/2+7/2	39571.326±0.009	0.14	3+4	38049.612±0.006	0.24
		7/2+9/2	39571.333±0.009	0.18	4+5	38049.687±0.006	0.31
		9/2+11/2	39571.405±0.009	0.22
	5/2+7/2	3/2+5/2	39590.134±0.010	0.10	3+4	38088.436±0.006	0.24
		5/2+7/2	39590.209±0.010	0.13	2+3	38088.476±0.006	0.18
		7/2+9/2	39590.217±0.010	0.18
		7/2+9/2	49466.413±0.012	0.32	4+5	47566.765±0.007	0.25
		9/2+11/2	49466.461±0.012	0.21	5+6	47566.809±0.007	0.30
3+4	7/2+9/2	5/2+7/2	49485.197±0.012	0.11
		7/2+9/2	49485.247±0.012	0.32	4+5	47605.485±0.007	0.24
		9/2+11/2	49485.247±0.012	0.32	3+4	47605.496±0.007	0.19
	
		9/2+11/2	59361.394±0.014	0.32	5+6	57083.792±0.009	0.25
	11/2+13/2	11/2+13/2	59361.427±0.014	0.21	6+7	57083.820±0.009	0.29
		13/2+15/2	59361.427±0.014	0.21
		9/2+11/2	59380.166±0.014	0.12	5+6	57122.454±0.009	0.45
		7/2+9/2	59380.201±0.014	0.32	4+5
		11/2+13/2	69256.261±0.016	0.33
	13/2+15/2	13/2+15/2	69256.261±0.016	0.33	6+7	66600.683±0.010	0.25
		15/2+17/2	69256.285±0.016	0.20	7+8	66600.703±0.010	0.28
	
		11/2+13/2	69275.026±0.016	0.13	5+6	66639.307±0.010	0.46
		11/2+13/2	69275.051±0.016	0.33	6+7

measured at 512 points over a bandwidth of ~ 4 MHz. A function representing a Lorentzian shaped signal detected at the second harmonic and a linear baseline were simultaneously least-squares fitted to scans consisting of 1200 pairs of magnetic field off minus field on sweeps for a total integration time of ~ 30 minutes. The frequencies in Table 1 are the mean values derived from four such scans recorded with the frequency swept up and down on successive scans. The uncertainties are the quadrature sum of the statistical errors and a 10 kHz

systematic uncertainty derived from measurements of standard lines of OCS and HCN (mainly between 170 and 195 GHz).

III. ANALYSIS

The Hamiltonian for analyzing the microwave spectra of C_3N and C_4H consists of standard terms describing the rotation, spin-rotation, and hyperfine energies. It is identical to that for CCH (Gottlieb, Gottlieb, and

TABLE 3—*Continued*

N→N'	C ₃ N Frequency (MHz)		C ₄ H Frequency (MHz)	
	J=N+1/2	N-1/2	N+1/2	N-1/2
7→8	79151.01±0.02	79169.77±0.02	76117.43±0.01	76156.02±0.01
8→9	89045.59±0.02	89064.36±0.02	85634.00±0.01	85672.57±0.01
9→10	98940.02±0.02	98958.78±0.02	95150.39±0.02	95188.94±0.02
10→11	108834.27±0.03	108853.02±0.03	104666.56±0.02	104705.10±0.02
11→12	118728.31±0.03	118747.07±0.03	114182.51±0.02	114221.04±0.02
12→13	128622.14±0.03	128640.90±0.03	123698.21±0.02	123736.72±0.02
13→14	138515.73±0.04	138534.49±0.04	133213.64±0.02	133252.14±0.02
14→15	148409.07±0.04	148427.83±0.04	142728.77±0.02	142767.28±0.02
15→16	158302.14±0.04	158320.90±0.04	152243.61±0.03	152282.08±0.03
16→17	168194.94±0.02	168213.68±0.02	161758.11±0.03	161796.57±0.03
17→18	178087.40±0.01	178106.14±0.01	171272.25±0.01	171310.71±0.01
18→19	187979.52±0.01	187998.29±0.01	180786.03±0.02	180824.47±0.02
19→20	197871.35±0.01	197890.10±0.01	190299.43±0.01	190337.80±0.01
20→21	207762.78±0.07	207781.54±0.07	199812.39±0.02	199850.79±0.01
21→22	217653.84±0.08	217672.60±0.08	209324.92±0.05	209363.29±0.05
22→23	227544.50±0.09	227563.26±0.09	218837.00±0.06	218875.36±0.06
23→24	237434.75±0.10	237453.51±0.10	228348.60±0.07	228386.94±0.07
24→25	247324.56±0.11	247343.32±0.11	237859.71±0.07	237898.03±0.07
25→26	257213.93±0.12	257232.68±0.12	247370.29±0.08	247408.60±0.08
26→27	267102.82±0.14	267121.58±0.14	256880.35±0.09	256918.63±0.09
27→28	276991.22±0.15	277009.98±0.15	266389.84±0.10	266428.10±0.10
28→29	286879.11±0.16	286897.88±0.16	275898.75±0.11	275936.99±0.11
29→30	296766.49±0.18	296785.25±0.18	285407.06±0.12	285445.28±0.12
30→31	306653.31±0.20	306672.08±0.20	294914.76±0.13	294952.95±0.13

NOTE.—The relative intensities of a transition $N \rightarrow N'$ sum to 1, but only hyperfine components with intensities greater than 0.02 are tabulated. Frequencies that in terms of radial velocity differ by less than 0.075 km s^{-1} are averaged. The $N=1 \rightarrow 2$ frequencies of Güélin *et al.* 1972 and the data in Table 1 are included.

Thaddeus 1983) with the addition of a centrifugal distortion term $\gamma_D N(N+1) \mathbf{N} \cdot \mathbf{S}$ in the spin-rotation interaction (Veseth 1970), and for C₃N a term describing the quadrupole hyperfine interaction of the nitrogen nucleus. Only the rotational constant B , centrifugal distortion constant D , spin-rotation constant γ , and spin-rotation centrifugal distortion constant γ_D can be derived from our laboratory data, since the hyperfine splittings in the high rotational transitions studied amount to only a few kilohertz, and are entirely unresolved.

When B , D , γ , and γ_D are simultaneously least-squares fitted to the laboratory data in Table 1, the B values for both C₃N and C₄H are in excellent agreement with those determined by Güélin, Friberg, and Mezaoui (1982). The uncertainty in the value of D determined from the laboratory data is 40 times smaller for C₃N, and 30 times smaller for C₄H, than that from the astronomical data. For C₃N the spin-rotation constants are in good agreement, but the uncertainty in the astronomical value is smaller by a factor of 20. The γ_D term is required for a satisfactory fit to the C₄H laboratory data. The uncertainty in γ determined from the C₄H laboratory data is 13 times larger than the uncertainty in

the astronomical value and differs from the astronomical value by 2σ .

A set of recommended microwave constants for C₃N and C₄H were derived from a least-squares fit to the combined data in Table 1 and the $N=2 \rightarrow 1$ astronomical data of Güélin, Friberg, and Mezaoui (1982) (see Table 2). To avoid the assumption that the radial velocities of C₃N and C₄H are the same as that of other molecules, the radial velocity was treated as a free parameter in the analysis, and independent determinations of the velocity were thereby obtained: $V_{\text{LSR}} = 5.55 \pm 0.05 \text{ km s}^{-1}$ for C₄H and $5.66 \pm 0.07 \text{ km s}^{-1}$ for C₃N, in good agreement with the value 5.60 km s^{-1} derived by Güélin, Friberg, and Mezaoui on the assumption that C₄H and C¹⁸O have the same radial velocity in B335. As can be seen in Table 1, the C₃N and C₄H frequencies calculated with the recommended constants in Table 2 agree with the laboratory data to within 1σ , with one exception.

Finally, to make our data useful to astronomers a list of predicted frequencies for the strongest C₃N and C₄H transitions is given in Table 3. Although the laboratory data yield much more precise values of D than can be obtained from the astronomical data alone, the uncer-

tainty in D is the major source of uncertainty in the predicted frequencies above ~ 200 GHz.

IV. DISCUSSION

Two ways centrifugal distortion affects the spin-rotation interaction are (1) the reduction of the magnetic field produced by the rotation of the nuclei with increased stretching of the molecular bonds, and (2) modification of the electronic structure caused by distortion of the nuclear frame. For C_4H the second mechanism is responsible for the large value of γ_D since the contribution to γ_D by the first mechanism of about $-2\gamma_D/B$ is 10 times smaller than that measured.

One of the most interesting findings is that the concentrations of C_4H and CCH in the acetylene-rare gas discharges are comparable. The implication is that in laboratory discharges, as in astronomical sources, the decrease in concentration of the $(C \equiv C)_n$ -H radicals containing successively greater number of $-C \equiv C$ -units is small. Thus, the prospect of detecting C_6H in the laboratory (and in space) is promising.

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